

A Review On Heavy Metal Chromium (VI) Biosorption Moderated By exopolysaccharide Producing Microorganism

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Abstract- *Pollutants have created a need for entirely new environmental remediation technologies that are greener, cheaper, and more efficient to eliminate or reduce pollution. A branch of environmental biotechnology, bioremediation, is currently considered one of the most promising options. This generation takes advantage of the superior ability of microorganisms and plants to accumulate, detoxify, destroy or eliminate environmental pollution. For financial reasons, of particular interest are the biomass-rich species produced as a by-product of large-scale industrial fermentation, or the positive metallo-binding algae found in much of the ocean. Bioremediation ensures the transformation and/or removal of organic and inorganic contaminants, even when present at low concentrations. Exopolysaccharides (EPS) are extracellular carbohydrate polymers that are produced and secreted with the help of microorganisms and accumulate outside cells. Biosorption occurs entirely within the bacterial cell. EPS facilitates the sequestration of metal ions, ultimately preventing their penetration to the cell surface.*

Keywords- Pollutant, Bioremediation, Biomass, Microorganisms, Exopolysaccharide, Biosorption, Heavy metal

I. INTRODUCTION

The rapid growth of industries (leather, textiles, mining, electrical manufacturing, etc.) has created problems of chromium-contaminated areas. Chromium is one of those metals that can be either beneficial or fatal to biological systems, depending on its oxidation state and perception. Chromium below 100 ppm is an important non-toxic mineral as well as playing a useful role in both nucleic acid synthesis and lipid, glucose and amino acid metabolism. In contrast, chromium, especially hexavalent chromium (Cr⁶⁺), was put into a separate category because it has a high oxidation state with mutagenic and carcinogenic effects on various organic systems. As stated by WHO and Indian Organization for Standardization, 0.05 mg/l is the permissible level of Cr⁶⁺ in used water and the permissible limit for Cr⁶⁺ in industrial

wastewater is between 2.0 and 5.0 mg/l (El-Naggar, N.E.A., El-khateeb, A.Y., Ghoniem, A.A). Heavy metals are naturally occurring elements found throughout the earth's crust, but most environmental pollution and human exposure comes from metal mining and smelting, industrial production and use, and domestic and agricultural use increase and metal-containing compounds. caused by human activities such as the use of. Environmental pollution can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment resuspension, and evaporation of metals from soil and groundwater water resources. It has also been reported that natural phenomena such as weathering and volcanic eruptions contribute significantly to heavy metal pollution. Industrial sources include metal processing in refineries, coal burning in power plants, oil burning, nuclear power plants, high voltage power lines, plastics, textiles, microelectronics, wood preservation, and paper mills (Tchounwou PB et, al; 2012).

1. Biosorption

Is a method of rapid and reversible binding of ions from aqueous solutions, onto functional groups which can be present on the floor of biomass. normally, sorptive properties of biomass are generally examined for wastewater treatment especially when different treatment methods have failed (Izabela et al.,2013). An extensive array of biological materials, particularly microorganism, algae, yeasts and fungi have received growing interest for heavy metal elimination and recuperation due to their precise overall performance, low price and massive available quantities. Bacterial biomass has become famous due to their small duration, ability to grow below controlled situations, and their resilience to a large form of environmental conditions; furthermore, cheaper nutrient sources are quite genuinely available for microbes. metallic ions in solution are adsorbed immediately to bacterial surfaces through interactions with chemical functional groups which consist of carboxylate, amine, amide, imidazole, phosphate, thioether, hydroxyl, and other functional groups discovered in cell wall biopolymers.

Various mechanisms have been proposed for the microbial biosorption of heavy metals, e.g., transport throughout the cell membrane, biosorption with the aid of cellular walls and entrapment in extracellular capsules, precipitation, complexation and oxidation–reduction reactions. The employment of bacterial biomass for metal removal treatment of wastewater is perceptively cautioned through many investigators. At some stage in metal-microorganism interaction, the polarizable groups (e.g., phosphate, carboxyl, hydroxyl and amino groups) are liable for metal binding capacity and able to interacting with cations. through the elimination processes by microorganisms, chromium may be eliminated during three important methods, i.e., biotransformation, bioaccumulation and biosorption, the latter is advanced to different ones, with quite selective depending upon the binding ability of biological substances used as biosorbents. apparently, the biosorption technique can take place by living and dead biomass, but the living biomass has benefits, i.e., the metal may be eliminated during the growth, consequently eliminating the processes of microbial replica, drying and storage (El-Naggar, N.E.A., El-khateeb, A.Y., Ghoniem, A.A. et al.)

2. Biosorption isotherm models

The biosorption isotherm represents the connection between the quantity adsorbed through the use of a unit weight of sorbent and the quantity of solute remaining within the solution at equilibrium (Sud et al., 2008). Exploration of solid-liquid sorption system usually relies upon on equilibrium batch isotherm and dynamic non-stop flow system (Volesky and Holan, 1995). numerous isotherm models viz. Langmuir, Freundlich, Redlich-Peterson and so forth. were proposed and the experimental information are analyzed within the light of these models to understand the mode of interaction for a specific sorbate-sorbent pair.

Langmuir isotherm model: This model indicates monolayer adsorption of a sorbate at the surface of a sorbent having finite number of identical sites and once a site is occupied no further adsorption is possible there. So, it denotes a saturation value beyond which no adsorption can occur (Kocaoba, 2007).

Freundlich isotherm model: The model assumes that the ratio of the quantity of solute adsorbed on a given mass of a sorbent to the concentration of the solute within the solution isn't steady at distinctive concentrations. It gives a concept of surface heterogeneity and exponential distribution of active sites and their energies and does not expect any saturation of the sorbent through the sorbate.

Redlich-Peterson isotherm model: it is a mixed form of Langmuir and Freundlich isotherm model. The mechanism of adsorption depicted by means of this model is a hybrid one and it does not follow ideal monolayer formation (Redlich and Peterson, 1959).

3. Desorption

It is a process that improves bound sorbate from adsorbents, and in some cases provides an efficient way to reuse the same biomaterial for adsorption technology. The reusability of biosorbents correlates with their applicability in the biosorption era (Saeed and Iqbal, 2003). Although currently the least effective method of desorption alleviates the disposal problems associated with spent sorbents, it also reduces the time and energy required to prepare sorbent beds if biosorption processes are carried out on a commercial scale. save appropriately. column reactor. Desorption of heavy metals is usually performed using dilute mineral acids or chelating agents such as EDTA. Desorption is performed with the ultimate goal of concentrating the loaded metals in a concentrated form while maintaining the pristine condition of the biosorbent for reuse with little loss. Metal uptake in continuous cycles. The desorbent should be a high-quality biomass that causes minimal damage to the anatomical matrix and binding sites (Saeed and Iqbal, 2003), but recovery is dependent on the biomaterial and the desorbent used. increase.

4. Microbial Exopolysaccharides (EPS)

Exopolysaccharides (EPS) are extracellular macromolecules that are secreted as tightly bound capsules or loosely adherent mucus layers in microorganisms. Exopolysaccharides (EPS) are important metabolites synthesized and secreted by certain microorganisms in response to challenging environments such as pH, temperature, salinity, osmotic stress, and various contaminants. Survive in such an unfavorable environment. They are proteins, DNA, phospholipids, and high molecular weight carbohydrates (sugar residues) substituted with non-carbohydrate substituents such as acetate, glycerol, pyruvate, sulfate, carboxylic acid, succinate, and phosphate. is a compound. (J Angelin and M. Kavitha, 2020). The EPS of microorganisms has his two types, the capsular layer and the mucus layer.

Capsule EPS

Isalso known as "cell-bound EPS".It is thicker than the mucus layer. Capsule EPS is positioned to protect cells from adverse weather, dehydration, osmotic stress, and toxic

compounds within biofilm formation (Dobaraa et al., 2014). It is also a toxicity issue as it helps avoid phagocytosis.

Slime EPS

EPS is secreted outside the microbial cell and loosely bound to the cell surface to form a mucus layer (Sonawdeker et al., 2016). Also known as "Released EPS". They are disordered layers of mucus that surround the cell surface. Supports cell motility and nutrient uptake. It binds cells together, adheres to smooth surfaces, and aids in biofilm formation. In addition, it protects the cells from desiccation.

5. Morphology and functional properties of Bacterial Exopolysaccharides

Layers of surface-associated covalently bound polysaccharides, anatomically located as the outermost protecting of microorganism cells are known as capsule. they convey mucoid appearance to bacterial colonies grown on laboratory agar media. Exopolysaccharides produced with the aid of microbes may be commonly categorised via their biological characteristic into intracellular storage polysaccharides (glycogen), capsular polysaccharides which can be intently linked to the cell surface (Schmid et al., 2015). And extracellular bacterial polysaccharides produced by way of plants (as an example, cellulose, pectin and starch) algae (agar and carrageenan) and microorganism (alginate, dextran, gellan, pullulan and xanthan gum) are commonly used as food components for their gelling, stabilizing or thickening properties which is probably essential for biofilm formation and pathogenicity (Ramalingam, et al., 2014).

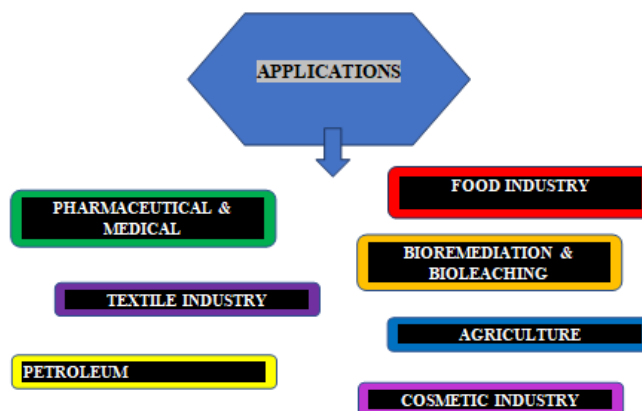
6. Role of Exopolysaccharides in aggregation

Aggregation in natural environment includes every biotic and abiotic strategies. In biotic process, live cell phytoplankton and microorganism is taken into consideration crucial for production of macro aggregates. As an example, macro aggregate, which have been basically clumps of bacterial cells glued together with the aid of EPS during microbial degradation of dissolved natural remember. In addition, mixture aggregate related microorganism make use of and convert DOM into fibrillar EPS that aids in aggregation. Manufacturing of TEP through living microbial cells is likewise considered an important mechanism of aggregation during phytoplankton bloom.

7. Application of Exopolysaccharides

There is lots of interest in microbial EPS and so, has an extremely good utility in numerous sectors because of its

various structure rheological properties and chemical composition.



The discoveries of numerous kinds of Exopolysaccharides have been noted. but most effective a handful has been proven to have food, pharmaceutical, biomedical, bioremediation, waste water treatment and bioleaching area their wide chemical, structural diversity and their physical, rheological, especially in regards to their use as biomaterials or as rheology modifiers of aqueous structures (Singh et al., 2017).

8. Chemical composition of Exopolysaccharides

EPS is comprised of repeating units of monosaccharide, which links with proteins (glycoproteins), lipids (glycolipids), acids (e.g., glucuronic acid, galacturonic acid, mannuronic acid), and/or extracellular DNA. EPSs nearly completely includes a confined quantity of different monosaccharide types or their derivatives and show a excessive diversity through numerous combinations of monosaccharide units that is organized in linear or branched configurations. The physicochemical properties and further applications of EPS depends on its emulsifying activity in different solvents, rheological behavior beneath varying pH. temperature and stress, gel strength, binding potential towards metals, ions, biodegradability, immunogenicity, nature, abundance (availability), and downstream processing (fermentation and commercialization). The maximum common backbone linkages of monosaccharide sequences are 1,4- β or 1,3- β -linkages, that exhibits characteristic structural rigidity, at the same time as other linkages plasticity, like 1,2 α - or 1,6- α -linkages are considered to have flexible structures. Extracellular polysaccharides are associated with each other and are capable of have interaction with other components of the EPS matrix. like proteins, lipids, inorganic ions, and other macromolecules of the bacterial cell surface.

9. Bacterial Biosorbents

In the early 1980s, various microorganisms were observed to accumulate high capacities of metallic elements (Vijayaraghavan and Yun 2008a,b). Since then, biosorbents derived from bacterial biomass have become famous for their small size, ability to evolve under controlled conditions, and resilience to a variety of environmental conditions. In addition, cheaper sources of nutrients for microbes are readily available.

Normally, very brief contact is sufficient for the metallo bacterial biomass to reach a steady state. This is because biomass is used in both fine powder and wet cell forms and mass transfer resistance is usually negligible. The fast dynamics seen in bacterial biomass is a major factor in the design of wastewater treatment systems.

Capsules and EPS produced by slime-producing microorganisms. In general, EPS have excess molecular weight and are rich in negatively charged functional groups (ligands). Eg., Carboxylic, hydroxy, and uronic acids (Sobeck and Higgins 2002; Yan et al., 2008). These ligands enable EPS to trap metal ions and form multiple complexes through electrostatic interactions (Pulsawat et al., 2003). Therefore, EPS was recommended as a metal absorber due to its very high ability to complex heavy metals (Gutnick and Bach 2000).

10. Mechanisms of Biosorption

Understanding the localization of metal deposition sites within biosorbed biomass and the metal deposition mechanisms combined with a description of the associated metal solution chemistry and the chemical structure of the metal deposition sites are all important in the search for efficient biosorption processes. It's the side. High metal selectivity and uptake are required. An interesting feature of biosorption is the particular specificity of biosorbents for divalent and polyvalent heavy metal cations. Metal uptake varies greatly between different genera and even different mutants within species. The nutritional state of the organism, its physiological state, the age and availability of micronutrients of the growing cells, and the environmental conditions (e.g., pH, temperature, and presence of other metal ions) during the biosorption process are all It is an important parameter that affects organisms. Performance of biosorbents. The solution chemistry of the metal also plays an important role in bioabsorption. Biosorption is caused by a variety of physicochemical mechanisms, depending on many external environmental factors, the type of metal, its ionic form in solution, and the specific active binding sites involved in

sequestering the metal. Biosorption consists mainly of various mechanisms such as ion exchange, chelation, adsorption and diffusion through cell walls and membranes, and depends on the species used, biomass origin and processing, and solution chemistry. Research is ongoing to establish biosorption as a commercially viable technique for metal capture and enrichment. Bioabsorption helps as a tool for recovering precious metals (e.g., from process solutions or seawater) and as a tool for removing toxic metals (especially from industrial wastewater). The driving force for ion exchange is primarily the attraction of the biosorbent to the sorbate (metal). Metals can bind electrostatically or by complex formation. The interaction between the solute (metal) and solvent plays a role in that less hydrophilic molecules have a lower affinity for the liquid phase and are therefore more readily adsorbed. Adsorption and microprecipitation are involved in binding electrically neutral metals without releasing stoichiometric amounts of previously bound ions.

In microprecipitation, the driving force is the interaction between solute and solvent, whereas in adsorption, the driving force is the affinity between adsorbent and sorbate. Microprecipitation does not necessarily involve bonding between biomass and metals. For physicochemical interactions based on physical adsorption, ion exchange and complex formation between metals and cell surface functional groups, metal uptake is independent of cellular metabolism. The mechanisms by which metals bind to cell surfaces most often involve electrostatic interactions, van der Waals forces, covalent bonds, or a combination of these processes. Negatively charged groups such as carboxyl, hydroxyl and phosphoryl groups in bacterial cell walls adsorb metal cations by electrostatic forces. (Tunali et al., 2006) show the bioabsorption of lead and copper by *Bacillus* sp. (ATS-1) including ion exchange mechanism. Since the main mechanism of biosorption is ion exchange, protons compete with metal cations for binding sites. Therefore, pH is the operating condition that has the greatest impact on the process (Schiewer and Volesky 2000). pH determines the protonation/deprotonation of metal ion binding sites and thus affects the availability of sites for sorbate. It is also possible to release the metal ion from the binding site by lowering the pH. This capacity is used for recovery of metal cations and regeneration of biosorbents.

11. Heavy metal: Chromium (presence in Environment and Industry)

Chromium (Cr) is a naturally occurring element found in the earth's crust with oxidation states (or valence states) ranging from chromium (II) to chromium (VI). Chromium compounds are stable in the trivalent [Cr(III)]

form, which occurs naturally in ores such as ferrochromite. The hexavalent [Cr(VI)] form is the second most stable state. The chromium element [Cr(0)] does not occur in nature. Chromium enters various environmental matrices (air, water, soil) from a variety of natural and anthropogenic sources, but the largest releases are from industrial activities. The industries that contribute the most to chromium emissions include metalworking, tannery, chromate production, stainless steel welding, ferrochromium and chromium pigment production. Increased concentrations of chromium in the environment are mainly associated with releases of chromium into the air and wastewater from the metallurgical, refractory and chemical industries. Chromium released into the environment from anthropogenic activities exists primarily in the hexavalent form [Cr(VI)]. Hexavalent chromium [Cr(VI)] is a toxic industrial pollutant and has been classified as a human carcinogen by several regulatory and non-regulatory bodies. The health hazards associated with exposure to chromium depend on its oxidation state and range from low toxicity for the metallic form to high toxicity for the hexavalent form. All compounds containing Cr(VI) were once thought to be man-made, but only Cr(III) is naturally ubiquitous in air, water, soil, and biological matter. However, recently, naturally occurring Cr(VI) was found in groundwater and surface water at levels exceeding the World Health Organization drinking water limit of 50 µg Cr(VI) per liter. Chromium is a pollutant in many environmental systems because of its widespread use in many industrial processes. Commercially, chromium compounds are used for industrial welding, chrome plating, dyeing and coloring, leather tanning, and wood preservation. Chromium is also used as a corrosion inhibitor in cooking systems and boilers (Tchounwou PB et, al; 2012).

12. Carcinogenic and Toxicogenic

The mechanism of biological interaction is unknown, and toxicity variability may be related to the ease with which Cr(VI) crosses the cell membrane and subsequent intracellular reduction affects reactive intermediates. There is. Chromium toxicity is primarily due to the Cr(VI) form, as Cr(III) is poorly absorbed by any route. It is absorbed from the lungs and gastrointestinal tract, and to some extent from intact skin. Cr(VI) reduction is considered a detoxification process when it occurs away from the target site of toxic or genotoxic action, whereas Cr(VI) reduction occurs within or near the target cell nucleus of the target organ. can help activate chromium toxicity. When Cr(VI) is reduced to Cr(III) outside the cell, no toxicity is observed because this form of the metal is not readily transported into the cell. The balance between extracellular Cr(VI) and intracellular Cr(III) ultimately

determines the amount and rate at which Cr(VI) enters the cell and exerts its toxic effects (Tchounwou PB et, al; 2012).

Cr(VI) enters many types of cells and is reduced under physiological conditions by hydrogen peroxide (H₂O₂), glutathione (GSH) reductase, ascorbic acid, and GSH, resulting in Cr(V), Cr(IV) to produce reactive intermediates such as thiyl radical, hydroxyl radical and finally Cr(III). Any of these species can attack DNA, proteins, and membrane lipids, thereby disrupting cell integrity and function. DNA strand breaks and urinary lipid peroxidation products have been observed in chromium-exposed workers, supporting signs of Cr(VI)-induced toxicity in humans. Oxidative damage is believed to be the underlying cause of these genotoxic effects, including chromosomal aberrations and DNA strand breaks. Nevertheless, recent studies indicate the biological relevance of non-oxidative mechanisms in Cr(VI) carcinogenesis. Carcinogenicity appears to be associated with inhalation of sparingly soluble/insoluble Cr(VI) compounds. The toxicity of Cr(VI) is independent of the form of the element. It varies greatly in a large number of very different Cr(VI) compounds. Epidemiological evidence strongly suggests that Cr(VI) is the carcinogenic active ingredient. The solubility and other properties of chromium, such as size, crystal modification, surface charge, and phagocytic capacity, may be important in determining cancer risk (Tchounwou PB et, al; 2012).

II. CONCLUSION

Bacterial exopolysaccharides are diverse, functionally rich, and their production is not restricted. Some of this diversity can be seen in monomer composition, binding linkages, and related conjugates, but functions can be summarized and applied as unique. Exopolysaccharides are produced as normal metabolic products of bacteria. Naturally occurring polysaccharides possess a unique combination of functional and eco-friendly properties.

Due to its versatile structure and function, EPS is used in many industrial and health applications. In an era of antimicrobial resistance, EPS has emerged as an effective antimicrobial agent, and more importantly, metal biosorption is an important application of EPS. EPS is known to sequester heavy metals such as chromium.

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